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Handbook for Analytical Quality Control in Radioanalytical Laboratories

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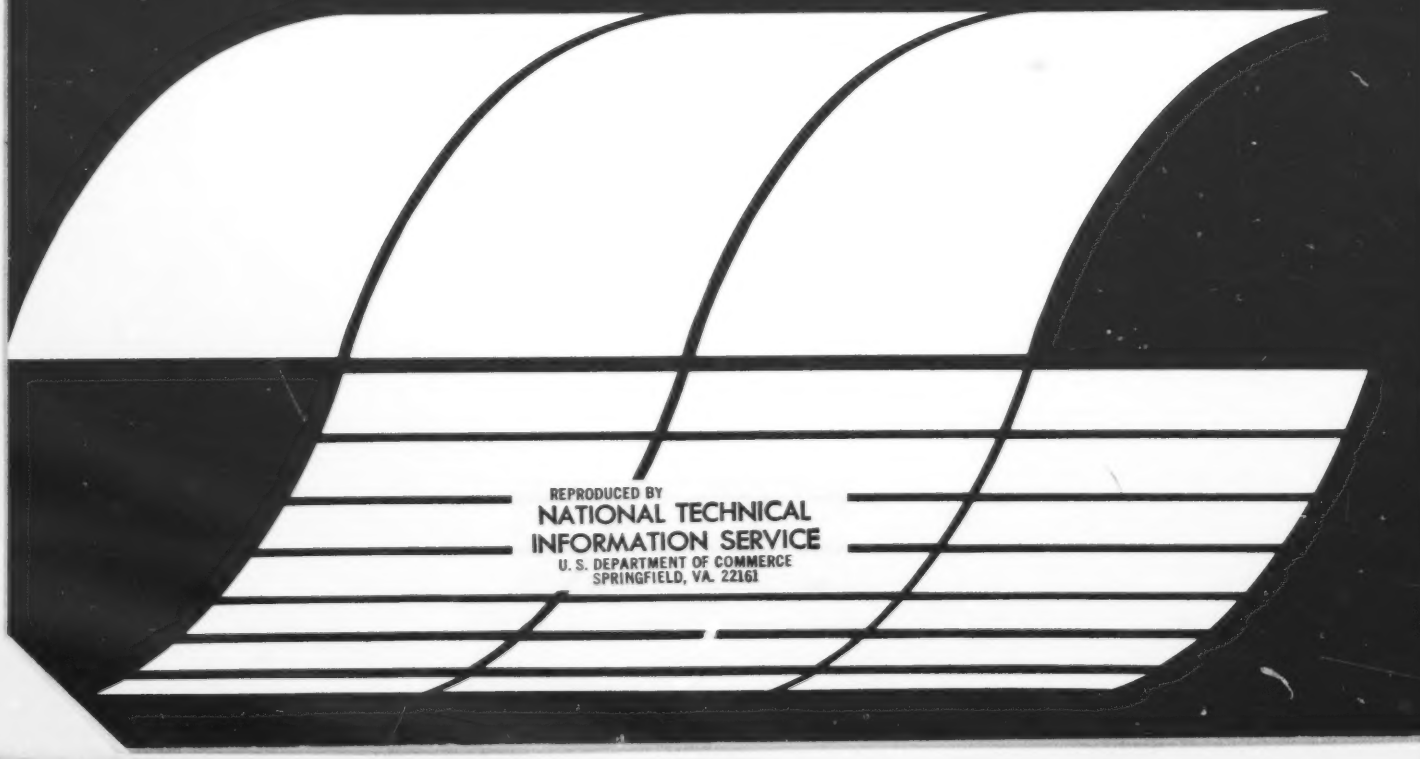

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Quality control in the radioanalytical laboratory is discussed. The discussion includes laboratory operating practices, analytical methodology, instrument quality control, and data handling and reporting. Two other sections on handling radioactive materials and counting statistics are included; these sections are brief and serve only as an introduction to the subjects.

The handbook provides methods for conducting internal and external quality control programs. Topics such as control charts, duplicate analyses, and routine spiked analyses are brought out.

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ABSTRACT

A basic responsibility of operating a nuclear power program is to establish an integral program for demonstrating the reliability and validity of analytical data taken in connection with the nuclear program. This handbook has been written for those persons who are responsible for producing radioanalytical laboratory data. The primary objectives are to identify the factors that can invalidate data and to provide guidelines for instituting a quality control program to monitor these factors.

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SECTION 1

INTRODUCTION

The role of an analytical laboratory is to provide qualitative and quantitative data that will assist in decision making. This is especially true in a program in which (1) laboratory measurements are used to indicate whether a given activity has significantly impacted the environment or (2) information is provided to determine whether operation of a specific facility complies with applicable regulations.

To be of value, analytical data must describe accurately the composition of samples submitted to the laboratory for analysis. A poor or incorrect result is often worse than no result at all. Further, a laboratory that is operated with no knowledge of its sources of variation and no procedures for action based on its results is not effective. Therefore, it is imperative that quality control be an integral part of any analytical laboratory program.

Although quality control is practiced to some degree in most radioanalytical laboratories, it occasionally is subordinated to pressures generated by a heavy workload and the need for rapid solutions to immediate problems. To be effective and useful, quality control must be built into a laboratory program to such an extent that it is a routine part of all other laboratory activities.

A quality control program should (1) ensure the accuracy and precision of data produced in the laboratory so that laboratory management can assess laboratory results in light of values known to be appropriate to the methodology and (2) maintain the quality of laboratory data continuously. Such a quality control program should cover personnel training, methods selection, equipment operation, and data handling procedures. A quality control program should provide sufficient information to demonstrate that all activities conducted by the laboratory fulfill the functions above.

This manual has a twofold purpose: (1) To introduce people of all backgrounds, who are new to radiochemistry and radiological counting instruments, to (a) special problems found in a radioanalytical laboratory (as well as good laboratory practices in general) and (b) advantages of quality control in their work; and (2) to provide a practical guide for professional radioanalytical personnel that will demonstrate methods for maintaining a higher degree of control in performing analyses and producing data. Detailed in this manual are (1) good analytical operating practices, (2) methods for evaluating analytical data to ensure accuracy and precision, (3) methods for identifying problems and improving data quality, (4) methods for ensuring that laboratory equipment is operating within specified control limits, with emphasis on alpha, beta, and gamma counting systems, and (5) methods of applying simple statistical techniques to document data quality.

SECTION 2

THE RADIOANALYTICAL LABORATORY

GENERAL

Section 2 describes the variables that an analyst must consider and control before he attempts to produce quantitative data. All laboratories have a large number of facilities, services, reagents, glassware, and sampling procedures that, although always considered quality control items per se, significantly affect the quality of data produced.

In the radioanalytical laboratory, the analyst must consider several unique factors if he is to perform radioanalytical determinations reliably, accurately, and precisely. Although certain factors, such as special air conditioning and reagent purity, normally are accounted for in any analytical laboratory, routine factors in the radioanalytical laboratory, such as natural background radiation, shielding, and floor loading, are not serious problems in other types of laboratory.

GENERAL LABORATORY ARRANGEMENT

Because a radioanalytical laboratory handles radioactive material in every aspect of its program, the laboratory must be designed to minimize employee exposure and cross-contamination of samples. The laboratory should be arranged so that radioactive materials are confined to one area or building, clearly designated as a "hot" area, to which access is restricted to authorized users of radioactive materials. Environmental laboratories can be protected from inadvertent contamination from adjacent areas of higher activity by (1) prescribed traffic flow patterns, (2) proper ventilation design to move air positively from low- to high-activity areas, and (3) good working rules and procedures. Laboratory employees must always remember that, although a spill of radioactive material may disrupt only one analysis, it could also cause a mandatory shutdown of the entire facility.[1]

Another important consideration is radioisotope storage. Radioactive sources should be stored so that the external radiation dose does not exceed applicable limits; normal storage is in a lead or lead-lined cave (vault). All dilution of radioactive materials to working concentrations should be performed in an isolated area. Each container should be labeled with the name and quantity of material contained and the appropriate dating information.

Counting instruments should be located in a room isolated from all other laboratory activities. This room should have sufficient shielding to provide a consistent radiation background at a level low enough to permit accurate determination of activities at the required limits of detection for the laboratory program. Generally, individual instruments rather than whole rooms are shielded. Floor loading due to heavy shielding and other operating considerations usually requires that a radioanalytical laboratory, or at least the counting room or rooms, be located on the lowest level of the building.

FACILITIES AND SERVICES

Distilled water is used in the laboratory for all routine laboratory operations.[2] However, the purity of ordinary distilled water is generally not sufficient for use in the radioanalytical laboratory since most counting techniques used in the radioanalytical laboratory are sensitive enough to detect very minute traces of radionuclide impurities. Specifically, water is often used for background determinations in gamma spectroscopy. Radionuclide impurities commonly found in distilled water could seriously impair analysis of low-activity samples. For determining background activity and other applications, distilled water must be further purified by passing it through a mixed-bed ion exchange column.[2,3] However, this process does not remove dissolved air, which may contain radon, or tritium, which is incorporated in the water molecules themselves. The deionized water used for background determinations in gamma spectroscopy must be stored for about 30 days to allow the short-lived daughter products of radon to decay.

The quality of compressed air required in the laboratory needs to be very high. Clean air should be produced at the compressor and maintained to the point of its use in the laboratory. Oil and water must be removed from the air supply. For radioanalytical purposes, the presence of radon gas in the compressed air must be considered. Although using tanks of compressed air that have been stored for 30 days or longer will reduce the radon concentration, the tank materials may contain small amounts of uranium or thorium, which by decay may produce a small but steady radon concentration in the compressed air. Of concern in some applications may be the presence of carbon-14 in the form of carbon dioxide in compressed air. This problem may be eliminated by using air manufactured by recombining nitrogen and oxygen.

An adequate electrical system, including both 115- and 230-V service, is indispensable for any laboratory. Many instruments require relatively constant voltage to maintain reliable operation. Lines that supply power to the counting room must be as noise-free as possible and should be used only for counting equipment. As necessary, individual line filters may be placed on various instruments. Laboratory lighting must be sufficient to allow detailed work and to provide comfort for employees.[4]

Counting rooms require special attention in the radioanalytical laboratory.[5] During initial construction only low-background materials should be used. Control of air conditioning and humidity is necessary: The temperature should be kept well below 30°C and should vary by no more than ±3°C, and humidity should be kept between 35 and 70%. High humidity may cause deterioration and arcing between components. Because fluorescent lighting can produce noise and interference in certain types of counting, incandescent lighting may be preferred; however, incandescent lights produce a large amount of heat. Counting rooms should be kept at a positive pressure relative to the laboratory and other parts of the building to minimize dust and fume concentrations and to protect against possible airborne contamination. In addition, the air conditioning system to the counting room should exchange the air five to ten times each hour.

GLASSWARE

Laboratory glassware is used in innumerable ways in every laboratory, but generally it is used to store reagents, measure solution volumes, and serve as reaction vessels. The principal glasswares used are Pyrex and Kimax, both of which are made from borosilicate glass, which is generally satisfactory for any analytical work. Recently, the use of Teflon, polyethylene, and polypropylene has become more common, but the limitations and advantages of these materials must be considered before use. For specific information on the properties of these materials, the reader should refer to the catalogs of the manufacturers.

Volumetric glassware and its proper use are important factors in many laboratory operations. For accuracy, the apparatus must be read correctly; that is, the bottom of the meniscus should be tangent to the calibration mark. Because fluctuations in temperature can cause expansion and contraction of glassware and solution volumes, glassware should be used only at the temperature for which it has been calibrated unless volume correction factors are known. The analyst should never assume that newly received glassware is accurate to the limits marked on it; new volumetric glassware should be thoroughly checked to ensure that it does meet specifications before it is used in routine work.[6]

Any good text on quantitative analysis[7] describes the techniques particular to various pieces of glassware. The analyst should be aware, however, that the notations "TC, to contain" and "TD, to deliver" that commonly appear on analytical glassware mean exactly what they say; if the two types are used interchangeably, laboratory results may be greatly reduced in quality. A "TC" pipet holds the exact amount of solution stated on the calibration and therefore should be emptied completely for accurate transfer. A "TD" pipet, when emptied, delivers the exact volume shown on the calibration; any residual solution should not be forced out of a "TD" pipet.

Glassware used for measuring liquids must be clean so that the film of liquid never breaks at any point when the glassware is being emptied. The required amount of solution will not be delivered nor will the amount delivered be reproducible if this precaution is not taken.

The method of cleaning will depend on the use to which the glassware is to be put and on the residue present from previous use. The first rule in keeping glassware clean is to rinse it thoroughly with water immediately after use since cleaning becomes much more difficult after the glassware has dried.

Volumetric glassware can be cleaned by several methods. One solution for normal cleaning is 30 g sodium hydroxide, 4 g sodium hexametaphosphate, and 8 g trisodium phosphate in 1 liter of water.[6] For more stubborn residue, a chromic acid solution may be used. Caution should be taken since this is a very powerful oxidizing mixture. Chromic acid solution is prepared by adding 1 liter of concentrated sulfuric acid to 35 ml of saturated sodium dichromate solution; this addition should be made slowly and with stirring

because a large amount of heat is evolved. The solution is then added to dirty glassware and allowed to stand for about 15 minutes. Glassware must be rinsed thoroughly with tap water, then rinsed with distilled water, to remove all traces of chromic acid. The chromic acid solution can be returned to a storage bottle for reuse. When the mixture becomes too dilute or turns a greenish color, it is no longer effective.

Greasy residue can be removed by soaking the glassware in acetone or by allowing warm sodium hydroxide solution to stand in the vessel. Again, care must be taken since sodium hydroxide can etch glassware. To dry glassware, rinse with acetone and blow or draw clean air, free of grease and oil, through it.

In a radioanalytical laboratory, it may be advantageous to use disposable pipets in procedures that may result in contamination. For small volumes, the automatic pipets with disposable tips are often used. Glassware used in work involving (1) high levels of activity or (2) environmental or low-level activity should be well segregated and clearly labeled to prevent cross-contamination; for example, this glassware should be washed in different laboratory stations. At times it may be best to throw away glassware used for work with high levels of activity rather than risk possible contamination of other samples.

LABORATORY INSTRUMENTS

Not as many common instruments are used in radioanalytical laboratories as in general laboratories. Equipment such as balances and pH meters must be checked and standardized regularly. The pH meters should be standardized daily with two buffer solutions that bracket the pH range to be used in laboratory work. Buffers obtained from chemical supply houses are satisfactory for routine use.

If balances are to be used only for measurements of difference, they need only be stable. A schedule of routine measurements on a set of known weights will indicate the proper stability. Normal precautions and maintenance must be used to achieve true weighings and ensure proper balance function. Certainly, an instrument logbook, containing records of all test weighings and balance servicing, should be maintained for each balance.

EXTRANEOUS COUNTS

The most difficult problem of the radioanalytical laboratory is to isolate the radiation emitted by a specific radionuclide from all other sources (extraneous counts). Extraneous counts can originate from background radiation or interferences from other radionuclides in the sample.

Background radiation usually is accounted for by measuring a simulated sample or source that is identical to an actual sample except for the relative absence of radioactivity. This technique can simulate those counts arising from environmental radioactivity (e.g., ^{40}K and decay products of the ^{238}U and ^{232}Th series), radioactivity in the detectors themselves,

cosmic rays, or electronic noise. The basic assumption in this technique is that background is stable (constant over a period of time) and that the only fluctuations that occur result from the statistics involved in the radioactive decay process. Actually, background often has a larger variability than predicted solely by counting statistics.[5]

To reduce fluctuations and further stabilize background contributions, shielding is necessary. Thick shields of selected lead or steel with graded liners will reduce measurably the background arising from environmental radioactivity. Background can be reduced further by using anticoincidence counting techniques.

Background contributions from environmental sources are exemplified by radon daughters, decay products of the ^{238}U series. Radon is always present in the laboratory in concrete block walls, compressed air, water, and often in the samples themselves. Therefore, the laboratory can attempt only to reduce the effects of radon fluctuations as much as possible.

Interferences can be caused by other radioisotopes in the sample that are present originally or introduced during sample processing. Errors encountered from this type of contamination may be reduced by carrying a "blank sample," a sample having no known activity, through the total analysis. However, for the situation in which more than one radionuclide in the sample may be of interest, the components or their decay products, which cannot be eliminated, may interfere with each other. If the interferents are different elements, chemical separation is possible; if they are isotopes of the same element, the interferents may be distinguished by a physical technique.

Other techniques that can be used to resolve interferents are selected on the basis of the half-lives of the radionuclides or the type and energy of radiation. For example, in a strontium analysis, the determination of ^{85}Sr in the presence of other strontium nuclides would present no difficulty because it is a gamma emitter, whereas ^{89}Sr and ^{90}Sr are beta emitters. Further selectivity can be exercised by using coincidence techniques. For example, because ^{131}I emits beta and gamma radiation, in cascade, it can be selected from other iodine radionuclides by applying coincidence techniques that choose the related ^{131}I emissions. Use of such a technique also yields sensitivities much greater than those possible by normal counting methods because the background is reduced to near zero.

Overall, extraneous counts generated by interfering radioactivity can limit the accuracy attainable in any analysis. Corrections depend on the degree of separation possible and the reproducibility of the separation. Nevertheless, statistical fluctuations from the interferent will introduce errors in the final result just as do background variations.

SAMPLING

The sample collector must ensure that samples are collected properly and transmitted to the laboratory in a condition acceptable for producing meaningful results. Therefore, the sample collector must start with a clear understanding of the purpose of the samples he is collecting and the manner in which the sampling program has been designed to meet this objective. From this starting point, one can determine what samples must be taken and what frequency of sampling is necessary to yield a true picture.

Samples collected by poor procedures always produce poor results. Accuracy and precision of the analytical procedures in the laboratory cannot compensate for an inaccurate sample (i.e., one that does not reflect the actual situation). The analyst must identify unsatisfactory samples when they are received and discuss, with those persons responsible for sample collection, the reasons for discarding the sample.

No attempt to discuss the varying methods of sample collection and treatment will be made since everyone experiences slightly different situations. Each sampling program may require different methods. However, procedures that are standardized and accepted by other laboratories in the field of study should be used. Sources of sampling information include HASL Procedures Manual,[8] Environmental Radioactivity Surveillance Guide,[9] Nuclear Regulatory Commission (NRC) Regulatory Guidelines,[10] American Society for Testing Materials (ASTM) Guidelines,[11] and Recommended Methods for Water-Data Acquisition - Preliminary Report of the Federal Interagency Work Group on Designation of Standards for Water-Data Acquisition.[12]

SAMPLE HANDLING AND TREATMENT

Once a representative sample is collected and delivered to the laboratory, the laboratory staff is responsible for properly treating and storing the sample. Often samples collected in an environmental survey require treatment because they are not physically ready for analysis. Treatment of the sample after it is received depends on the sample itself and the analyses to be performed on it. Most treatment and handling techniques have been established and well known for many years. Again, certain precautions must be taken in the radioanalytical laboratory.

Water Samples

Generally, water samples should be acidified when collected. Under certain conditions this procedure should be modified; for example, if total and dissolved fractions are to be analyzed, the samples should be filtered before acidification. If tritium or carbon-14 analyses are to be performed, portions for these analyses should be separated before acid is added. Samples for tritium analyses should not be stored in polyethylene bottles for more than 3 or 4 months because water can evaporate through the polyethylene. If the samples are to be stored for any length of time,

carrier or complexing agents should be added to prevent adsorption of trace metals on the storage containers. Adsorption is known to occur quite rapidly under some conditions.

Air Filters

The air filter should be handled with care when dust loading is observed because particulate matter is easily removed from the filter, thus invalidating the analysis. Air filters are often received by the laboratory in envelopes; some extremely low-level analyses may require analysis of the envelope in which the sample arrived as well as the sample itself.

Milk

Milk samples should be refrigerated until analyses can be performed. If the analyses will be delayed for more than a few days, a preservative (formalin or merthiolate) should be added to inhibit bacterial growth and retard spoilage. Milk samples that are to be analyzed for ^{131}I should not have formalin added because formalin is thought to cause increased complexing of the iodine.

Soil

Soil samples should be dried, pulverized, and sieved to pass a 200 mesh (this will vary according to the analyses to be performed) sieve before analysis. Further thorough mixing is required to ensure a homogeneous sample.

Other Samples

Perishable samples should be preserved by refrigeration or freezing. Vegetation and other samples may need to be dried, pulverized, or ashed before analysis.

PERSONNEL TRAINING

Although the degree of skills and training necessary for laboratory personnel naturally corresponds to their job responsibilities, all laboratory personnel must be thoroughly acquainted with basic laboratory operations. A new laboratory analyst must learn (1) how the sample processing system of the laboratory works so that he is familiar with the laboratory's unique sequence of work; (2) how each type of sample is to be treated when it arrives in the laboratory; (3) how to use routine laboratory equipment such as volumetric glassware and analytical balances; (4) how to clean glassware properly; and (5) how to maintain routine equipment of the laboratory such as pH meters and balances.

Before a new analyst is assigned to independent work, a gradual on-the-job training program should be conducted. The trainee should first observe experienced personnel at work and study the laboratory manual thoroughly. The trainee should then perform the analysis under close supervision of an experienced analyst. Finally, the analyst should be allowed to work independently, but his work should be checked frequently at first. Provision should also be made to retrain each analyst regularly, especially in any areas in which he does not perform often.

The work in the radioanalytical laboratory ranges from sample preparation to simple analyses, such as a gross beta analysis, to complex analyses, such as strontium or plutonium separations. The time necessary to train an analyst properly increases with the difficulty of the analyses expected of him. Several months of training may be necessary before a new analyst can perform independently all the types of work required of him.

The most difficult task in the radioanalytical laboratory is to operate the counting equipment properly. This job is complicated because the operator must be able to detect invalid data early to avoid large wastes of counting time and analytical effort. For example, the examination of raw gamma spectroscopy data to ensure an adequate measurement is a very subjective art. The operator will have to see hundreds of samples under all conditions before he can judge data effectively; this will require many months of experience.

OTHER ITEMS

Another factor that must be considered when planning the radioanalytical laboratory program is the half-life of radioactive materials. Samples must be analyzed soon after they are received to ensure accuracy and low error estimates for radionuclides that have half-lives of only a few days. Half-life considerations require that the laboratory have a program for continuously renewing its supply of calibrated material. Most standards are assumed to be invalid after passing through four half-lives from the date of certification because of compounding of errors and assumptions made in the original determinations of half-lives for the various radionuclides.

Quantities of material needed or available for analysis have a significant role in the work of the laboratory. Large samples are necessary for working with low-level radioactivity to provide sufficient activity to count; however, large samples reduce the efficiency of a gamma counting system because of the poor counting geometry and introduce possible interferents into the analysis. Therefore, the sample size must be considered when computing the overall analytical error. The problem of sample size often is more pronounced for the radioanalytical laboratory because of the isotopic abundances of some radionuclides. For instance, the abundance of ^{40}K is about 1/100 of one percent of the total natural abundance of potassium. Whereas an analyst in a general laboratory would analyze for total potassium, the analyst in a radioanalytical laboratory may determine only the ^{40}K content of the sample.

Samples containing high levels of radioactivity may require dilutions to avoid counting errors in gamma spectroscopy caused by dead time of the multichannel analyzer system. Here again the radioanalytical laboratory has a more pronounced version of the problem since a sample may have a very high activity, but a very low initial concentration of the nuclide of interest. Dilution simply amplifies the problem. Usually, carrier must be added to the solutions to keep the radionuclides of interest from absorbing on the container walls at their low concentrations. Chemical separations can always be performed, but if the analysis can be performed by gamma spectroscopy without chemical separations, a significant cost savings can be effected.

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SECTION 3

QUALITY CONTROL OF COUNTING EQUIPMENT

GENERAL

Most chemical laboratories can switch to a strictly wet chemical approach to avoid instrumentation problems, but virtually all measurements in a radioanalytical laboratory eventually require the use of counting equipment for final determinations. A number of quality control measures are necessary to ensure proper instrument performance. Specific quality control procedures to be followed depend on the type of radiation being analyzed and the methods of detection and signal processing used. Such procedures will be discussed in this section.

TYPES OF COUNTING EQUIPMENT

Virtually all analyses in the radioanalytical laboratory eventually require the measurement of alpha, beta, or gamma radiation. In general, each type of radiation is analyzed with different types of equipment of a highly specialized nature, all of which can detect a low-level signal, amplify it, process it, and store or record it as digital information.

Alpha radiation can be counted in several different ways, depending on the type of information and degree of sample handling desired. For a sample that has undergone chemical separation to eliminate interfering radionuclides and deposition as a thin layer in a counting geometry, counting can be performed using either an internal proportional counter (IPC) or a thin-window gas-flow proportional counter. (In an IPC, the sample to be counted is actually introduced into the counting chamber of the detector itself. The sample is outside the detector in a thin-window gas-flow proportional counter; therefore, the beta or alpha emissions must penetrate through the detector window to enter the counting chamber.) Selection of the instrument to be used for a particular analysis is based on the counting efficiency and sample-processing speed desired. The IPC can normally achieve a counting efficiency approaching 50 percent for alpha and beta radiation, but it is relatively inconvenient for processing samples rapidly because most IPCs have no automatic sample changers.

In general, the thin-window gas-flow proportional counter is preferred for most gross counting of alpha and beta radiation. Most newer models are dual-detector instruments operated in the anticoincidence mode. The instruments are capable of achieving efficiencies (corrected for self-absorption) of greater than 20 percent for alpha (^{210}Po) radiation and greater than 40 percent for beta (^{90}Sr) radiation while maintaining a background of less than 1.4 counts per minute. Also, most modern instruments have automatic sample changers with capacity for at least 50 samples.

Isotopic analyses of alpha-emitting radionuclides can be made by alpha spectroscopy. Alpha spectroscopy is especially useful for analyzing uranium milling and mining materials, which have a large number of alpha-emitting radionuclides present. The nuclides of interest must be chemically separated and then electroplated onto a small metallic disc. The alpha emissions from thin sources are detected by surface barrier detectors, and the data are collected with a pulse-height analyzer (PHA); however, all sources must be electroplated to achieve any reasonably reproducible resolution for the instrument.

Activities of samples that emit low-energy beta particles such as tritium and carbon-14 are usually determined by liquid scintillation counting. Liquid scintillation counting can be a rapid and sensitive technique, but it usually requires some type of purification of the sample to prevent quenching. Some alpha and X-ray counting can be done by liquid scintillation.

A scintillation system composed of a nylon disc coated with an activated zinc sulfide (ZnS) phosphor also may be used to count alpha and beta radiation. The sample is placed on the disc and counted with a photomultiplier tube. The counting system must be in a lighttight container.

Radium-226 is often determined by the technique of radon emanation. In this technique, a radium-226 solution is stored in a sealed container for 15 to 30 days to allow its daughter product, radon-222, to grow into the sample. The radon is then transferred to a ZnS (silver-activated) coated counting cell called a Lucas cell. The alpha emissions of radon-222 and its daughters produce light pulses, which are counted with a photomultiplier tube. This technique has a counting efficiency approaching 70 percent. Again, the counting must be performed in a lighttight container.

Gamma radiation can be counted with many different instruments; however, the two basic categories are single- and multichannel analyzers. If a specific photopeak of a particular radionuclide is easily isolated and if the sample contains no other radionuclide that can affect the counting, a single-channel analyzer and scaler can provide all the information needed for one analysis.

The more common analytical problem is the analysis of a sample that possibly contains a wide range of radionuclides, any or all of which may be of interest. In this type of application, gamma spectroscopy with a PHA system yields the most informative estimate of the activities of several radionuclides. There are basically two types of detectors now being used for gamma spectroscopy: the thallium-doped sodium-iodide [NaI(Tl)] detector and the lithium-drifted germanium [Ge(Li)] or the intrinsic or hyperpure germanium (HPGe) detector.

An analysis system based on a 10- by 10-cm NaI(Tl) crystal typically requires an analyzer with at least 256 channels of memory and at least one readout device. A shield with a minimum of 10 cm of steel or its equivalent is necessary to achieve acceptable background levels for environmental monitoring.

A germanium-based analysis system requires a much more sophisticated multichannel analyzer, with at least 2000 channels of memory and one high-speed readout device. Normally, a 4000-channel analyzer is a better selection to fully utilize the improved resolution of newer germanium detectors. Many analyzer systems available today for germanium analysis are computer-based systems having 24 to 128K of usable memory. Because these systems have their own analysis software capability, the user is completely independent of external computer requirements.

The activity levels being determined in different laboratories or within the same laboratory can vary extensively. Counting samples that contain low levels of activity requires counting equipment with extremely low noise and high selectivity, and counting of high-activity samples requires equipment with exceptional response and low distortion. Therefore, the instruments must be of the highest quality and versatility.

STANDARD CHECK SOURCES

A specific check source should be used with each counting system. A source chosen as a check will contain a nuclide or nuclides whose type and energy of radiation correspond to the type of analysis for which the counting system is to be used. This source will be counted routinely to determine general performance of the system and to ensure that the efficiency of the system has not changed. Although knowledge of the absolute activity of the source is not necessary, the source must be sufficiently active to provide adequate counting statistics over the time for which it is to be counted. However, the source must not be so active as to cause pulse pileups, dead time that is significantly different from that to be expected from routine samples, or gain shift in the case of PHA systems. For example, a check source for a PHA system, equipped with a modern analog-digital converter (ADC), should not count a total rate exceeding about 1000 counts per second. Any source to be used as a check source should be either sealed or encapsulated to prevent loss of the source and contamination of the counting system. The check source-to-detector geometry must be known and held constant. The geometry is extremely important because small changes can have large effects that overshadow normal statistical counting variations.

Because alpha and beta sources are subject to leakage after a few years, they should be replaced periodically even though the nuclide may have a long half-life. Also, alpha and beta sources should be surveyed (smeared) routinely for possible leakage.

INSTRUMENT CONTROL CHARTS

The statistical nature of radioactive decay will result in uncertainties in the determinations of check and background count rates. Despite this effect, the analyst is able to detect deviations

from the "true" values that result from instrument malfunctions by recording routine check-source and background determinations on control charts. Quality control charts initially were devised to follow graphically the quality control of manufactured products by testing a limited sample to determine whether reproducible results were being obtained. This same principle can be applied to any type of repetitive measurements.[1-3]

A control chart consists of a graph showing time on the abscissa and count rate, or total counts, on the ordinate. Lines are drawn parallel to the time axis at values (corrected for decay if necessary) for the "true" count rate and for values of ±2 and ±3 standard deviations. The "true" count rate is determined by averaging at least 20 countings whose individual statistics are acceptable, or from a single measurement for a longer period, such as an overnight count. When multiple measurements are to be made and averaged, the limits of the quality control chart must be corrected appropriately. For example, for a control chart based on the average of three measurements, the ±2 and ±3 standard deviation limits must be divided by the square root of three to yield appropriate values.

Quality control charts must be interpreted objectively. When a point goes outside the limits, instrument service may or may not be needed. To determine whether service is necessary, the analyst should run a series of repeated measurements and apply another statistical test, such as a Chi-square test, to determine whether the variation was nonstatistical.[4]

Trends from control charts may show other information. For example, if regular measurements of the check source are daily moving in one direction, one can infer that some system variable is changing. This variation may not always require instrument service; instead, reevaluation of the values of the standard deviation and other related limits of the control chart may be necessary.

ALPHA AND BETA COUNTING

On a daily basis (or before each use), the check source for each system should be counted for a predetermined time. The count rate is entered in the logbook and plotted on the control chart established for the specific system. This value is compared with the ±2 sigma (warning) limits and the ±3 sigma (out-of-control) limits, and the procedure is repeated if the ±2 sigma boundary is exceeded. Sustained values above the warning levels require appropriate action.

On a daily basis (or before each use), background for each system should be counted for the standard counting time (the time for which samples normally are counted) if overnight background counts are not made. Background measurements obtained during the same period in which actual sample measurements are being made are preferable. This value is entered in the logbook and plotted on the control chart established for the specific system (Figure 1). The value is compared with the ±2 and ±3 sigma limits, and appropriate action is taken if indicated.

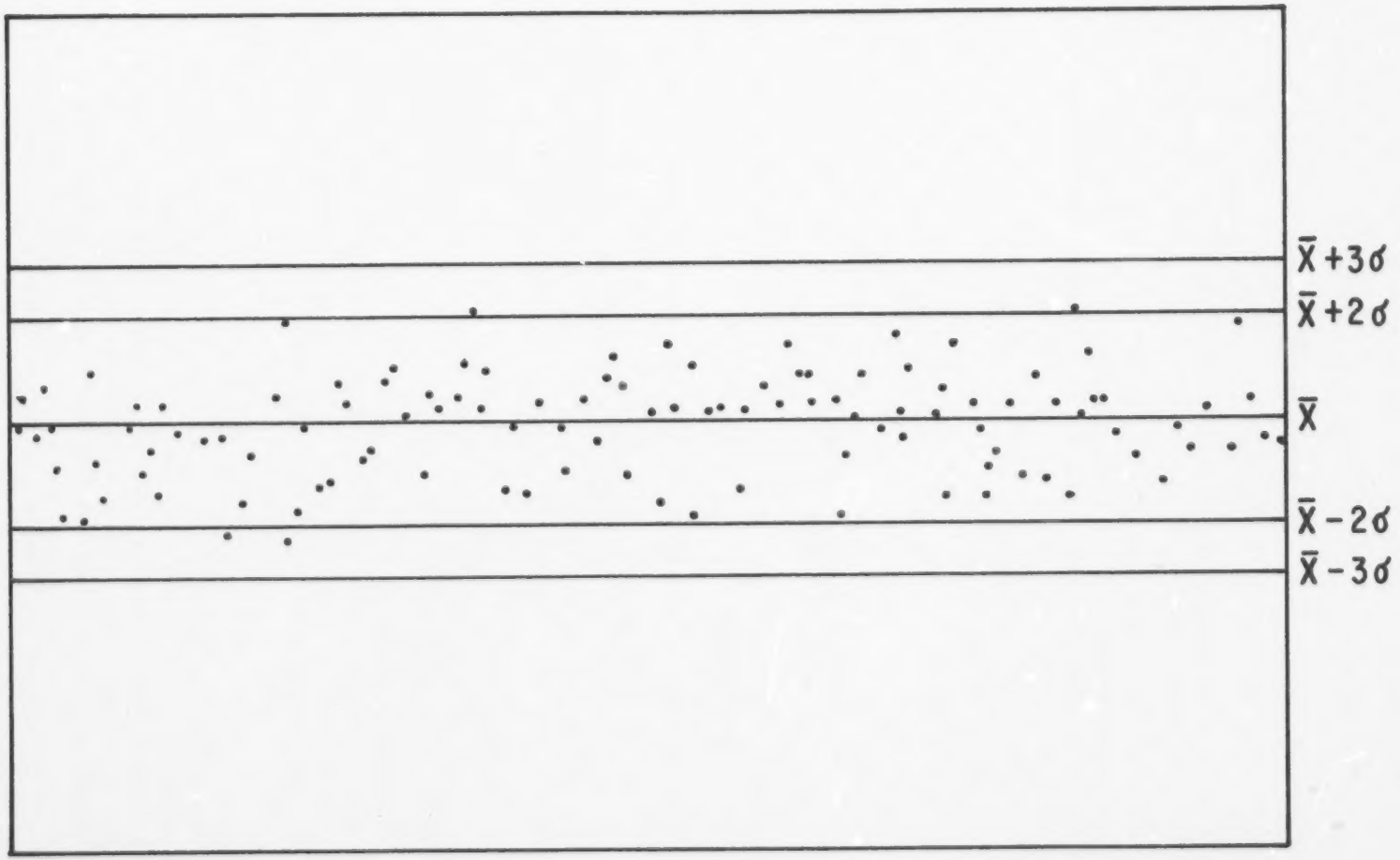

Figure 1. Control chart for daily measurements of background radiation.

Appropriate action for background or efficiency changes includes:

1. A check of the source positioning or for possible contamination.

2. A check of the gas supply for possible variation in the gas pressure.

3. A check of the gas itself; bad gas usually is indicated when several instruments operating off the same supply change drastically at the same time.

4. A check of the high-voltage (HV) setting to determine whether drift or other factors have caused the HV to change from the correct operating potential; also check the HV actually delivered to the detector.

5. A thorough cleaning of the detector to remove possible contamination from the window or sample chamber.

6. A check of the line volage to determine whether noise is entering from the power source.

7. A check of the instrument preamplifiers and other signal processing circuits for proper functioning.

8. A check of the instrument guard detector (if a dual-detector system) for proper functioning.

9. A check of cabling and grounding to determine whether the HV is arcing.

Certainly this list is not all-inclusive, and other checks should be identified by the laboratory staff as part of a routine check-off procedure when malfunctions occur.

The control charts should be reviewed each week for possible trends. If trends are present, the cause should be determined and appropriate action should be taken.

On a quarterly basis or after electronic repair or modification, the detector plateau for gas-discharge devices should be determined and plotted. Some laboratories prefer to redetermine plateaus after each change of counting gas, although this may not be necessary if the check source counts normally. All pertinent instrument settings, the source used, and the rate of gas flow should be recorded on the plateau graph, which should be attached permanently to the logbook. From this plateau, the operating voltage is selected or verified and the plateau slope at the operating point is calculated. The slope should generally not exceed 2 percent per 100 volts for a ^{90}Sr source. The operating potential is usually selected as the midpoint of the plateau. Thereafter, the HV setting should be checked for drift once every two months.

The percentage of alpha-beta crossover should be determined periodically for those systems in which alpha radiation is differentiated from beta radiation by pulse-height discrimination. Window settings are then adjusted as necessary to minimize crossover.

GAMMA COUNTING

Due to differences in signal processing, methods for use in gamma counting are divided into two classes: single-channel analysis and multichannel analysis.[5,6]

Single-Channel Analysis

The selected check source should be counted over the energy window of interest for a predetermined time each day or before each use. The amplifier fine gain is adjusted for optimum response before this measurement. The total counts in the window are then entered in the logbook and plotted on the control chart established for the specific system. This value is compared with the ±2 sigma and ±3 sigma limits, and the measurement is repeated if the ±2 sigma limit is exceeded. Sustained values above the warning limits require appropriate action.

A background count should also be made over the same energy window of interest for the standard time required for sample counting if overnight background counts are not made. The total counts in the window are entered in the logbook and plotted on the background control chart established for the specific system. This value is compared with the ±2 and ±3 sigma limits, and appropriate action is taken if the limits are exceeded.

Occasionally, or when anomalous background measurements are observed, the analyst may perform a Chi-square test to determine whether the performance is statistically acceptable (see Section 6). Too small a value of Chi-square indicates some regular interference such as 60-hertz noise, and too large a value of Chi-square indicates malfunctioning electronics.

Appropriate action for background or efficiency changes includes:

1. A check of source positioning or for possible contamination.
2. A check of energy window settings, including possible changes of window size that are not reflected on the actual dial settings.
3. A check of gain settings.
4. A check of the preamplifier for noise and malfunction.
5. A check of the HV settings of the detector and HV delivery to the detector.
6. A check of the HV supply for noise.
7. A check of the check source geometry.

Because other possibilities exist, a good checklist should be prepared and consulted whenever necessary.

The control charts should be reviewed each week for possible trends. If trends are present, the cause should be determined, and appropriate action taken.

Multichannel Analysis

Before instrument efficiency or background counting rates are determined, the instrument must have a proper energy calibration; that is, a multiline reference source should be counted for a time sufficient to provide acceptable statistics. The channel positions of the spectral lines are adjusted with the appropriate PHA controls until the spectral lines correspond as closely as possible to the known line positions. A laboratory may wish to have more than one source for this check for NaI(Tl) detectors: (1) a check source, such as ^{207}Bi, that has several emission lines spread widely throughout the major regions of interest and (2) a source that has several lines in the low-energy (<300-keV) area, where linearity is most critical. For germanium detector systems, a check source, such as a multinuclide point source traceable to the National Bureau of Standards (NBS), can be used. Such a source has lines from about 300 keV, spaced at even intervals throughout the energy spectrum, to 1800 keV. From the channel positions of two or more specified lines appropriate to the energy region of interest, the energy by channel (keV/channel) and zero intercept are calculated and entered in the logbook.

After energy calibration, the selected check source should be counted for a predetermined time each day or before each use by using a selected energy window. The amplifier fine gain is adjusted to center a specified photopeak on a selected channel. The window can be set to measure either the total number of counts in the specified photopeak or the total number of counts summed over the number of channels, symmetrically disposed around the photopeak channel, that is equal to the full width at 1/10 maximum. The total number is entered in the logbook and plotted on the efficiency control chart established for the specific system (Figure 2). This value is compared with the ±2 and ±3 sigma limits, and the process is repeated if the ±2 sigma limit is exceeded. Sustained values above the warning limit require appropriate action.

Background should be counted for the standard counting time. The total counts in the energy window defined above for the efficiency test are entered in the logbook and plotted on the background control chart established for the specific system. This value is compared with the ±2 and ±3 sigma limits, and appropriate action is taken if the limits are exceeded.

Appropriate action for background or efficiency changes includes:

1. A check of source positioning or for possible contamination.

2. A check of the energy/channel value to determine whether a gain shift has occurred.

3. A check of gain settings.

4. A check of the preamplifier for noise or malfunction.

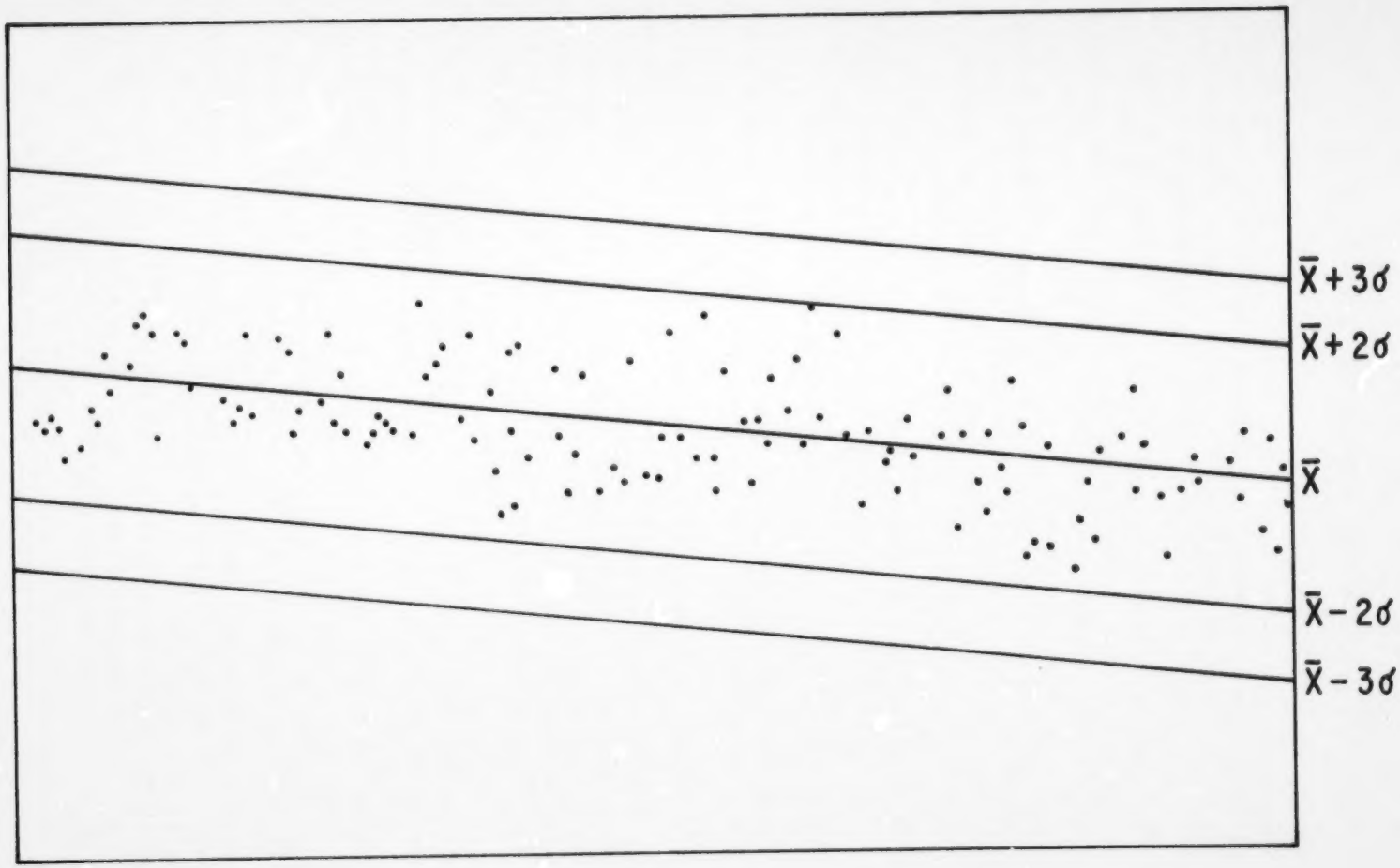

Figure 2. Control chart for the daily counting of a standard reference source; the chart is corrected for decay.

5. A check of the HV settings of the detector and HV delivery to the detector.

6. A check of the HV supply for noise.

7. A check of the counting geometry of the check source.

8. A check on the ADC performance.

Again, these suggestions do not constitute a complete list of possible checks; however, personnel in the counting room should compose a checklist for reference purposes when problems arise.

The control charts should be reviewed weekly for possible trends. If trends are present, the cause should be determined and appropriate action should be taken.

The resolution for a specified photopeak should be determined and recorded at least once a month. Changes of about 2 keV for NaI(Tl) systems require corrective action. At the same time the peak-to-Compton ratio should be determined and recorded in the logbook.

The integral energy linearity of the PHA system should be determined periodically with a multinuclide source covering the energy range of interest. The differential linearity of the multichannel analyzer should be determined with a sliding pulser at least twice a year.

Time bases should be checked regularly for proper functioning in all the time periods that will be used for analysis.

An energy efficiency curve should be determined annually for each germanium detector system for each geometry with a multiline reference source calibrated by the NBS. The curve for the most frequently used geometry should be checked frequently during the year. Complete information concerning the half-lives and decay schemes can be obtained from the nuclear data tables[7,8] if it is not provided by NBS with the source. For comparability, these same values should be used in any similar work. A check on the energy efficiency curve is not necessary for every geometry for quality control purposes. The EPA Environmental Monitoring and Support Laboratory in Las Vegas also offers well-characterized standardization material, which is available regularly.

By using a gamma ray source or sources that have energies ranging from about 100 to 1500 keV, the operator can estimate the status of a NaI(Tl) or germanium detector. Any degradation over time of the low-energy line would indicate that the surface of an NaI(Tl) detector is deteriorating or that the depth of the dead layer of a germanium detector is increasing. The status of the bulk volume of the detector can be estimated from the higher-energy lines.

A thorough and up-to-date discussion of the problems of quality control in gamma-ray spectrometry has been compiled by Zeigler and Hunt.[9] Specific tests and evaluation procedures, with sample data, are discussed at length.

To achieve meaningful data, these routine measurements of quality control must be made in an identical fashion every time. This will require formulation of extremely reproducible geometries, explicit instructions, and meticulous obedience to those instructions by all operators. Small daily changes in methods can result very quickly in values that may differ from earlier results by 50 percent.

Use of these routine procedures and others specifically drawn up by each laboratory will allow the operators to state with confidence whether a particular system is operating properly at any moment.

CALIBRATION

Instrument calibration with good standards should be performed regularly. Only well-defined standards should be used, and care must be taken to prepare samples homogeneously and in accurately defined geometries. Replicate samples, multiple measurements, and good counting statistics should be stressed as important for every geometry used.

If multiple detectors are run simultaneously by one multichannel analyzer, the operator must avoid acquiring data on high-activity samples from more than one detector at a time through the same ADC. Even though the analyzer corrects for dead time, the samples may contribute to the dead time by different percentages. Also, use of samples that have sufficient activity to cause spectral distortion should be avoided by using dilution as necessary.

REFERENCES

References 1, 2, and 3 discuss the construction of control charts, and references 4, 5, and 6 discuss some specific parameters that should be monitored by control charts.

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SECTION 4

ANALYTICAL PERFORMANCE

GENERAL

Maintaining a flow of accurate data from the laboratory in a program that involves a large volume of samples is difficult. A laboratory must first analyze the scope of its projected program to determine those factors that will influence the final results. Facilities, services, methods, equipment, reagents, chemicals, and training of personnel all have an impact on data quality.

Once a laboratory has competent analysts, reliable, properly operating equipment, and well-known tested procedures, quality control procedures can be used to (1) minimize systematic error in the total analysis and (2) document the quality of data produced by the laboratory. Although quality control cannot ensure absolute accuracy, it can help produce consistent data.

SELECTION OF ANALYTICAL METHODS

A number of chemical procedures and counting procedures are available for use in any radiochemical analysis. This multiplicity of techniques makes method standardization difficult and often indescribable since variations of a single procedure may be used in a laboratory for different types of samples. Also, this array of choices makes method selection difficult and requires that the analyst be able to document his choice of method and the validity of the results obtained with that method.

The analyst can be more confident of a particular method if it has been generally accepted throughout the industry. Therefore, when the laboratory staff plans to adopt new procedures, it should consider standard methods, particularly from ASTM, EPA, NRC, the American Public Health Association, and the Association of Official Analytical Chemists. These procedures should be studied to help determine, for a particular analysis, (1) the levels that can be measured precisely and accurately in the presence of known interferences; (2) the equipment and skills that are required to perform the analysis; (3) the size of sample load that can be analyzed by the method; and (4) the information that is available to indicate the validity of the method.

After the laboratory staff has accepted a method that fulfills the needs of the laboratory in terms of the above criteria, it should document that method carefully before it is used routinely. Proper documentation includes a write-up in a standard procedural format used for all analytical methods in the laboratory. Once the method is accepted, documented, and placed into use, it should be checked periodically to ensure that it continues to meet the needs of the laboratory. As these needs change over time, the adoption of newer, quicker, or more sensitive methods may be necessary.

Acceptance of a procedure should not stop investigations that might lead to improvements in the specificity or sensitivity of the method. Before such a modification is made, it should be worked out carefully and data should be accumulated to document the superiority expected from the modification. Before the new procedure is used routinely, it should be rewritten in the laboratory's standard procedural format to ensure that the procedure is followed correctly by the staff.

REAGENTS AND CHEMICALS

If all other factors in a laboratory are under control, the most important source of error remaining is the chemicals and reagents used to process samples. Control of chemicals and reagents is extremely important to any program.

The quality of reagents is of great importance. The type of reagent for a particular use is often determined by the impurities that can be found in the reagent. Generally, the best quality of reagent available should be employed. Chemicals that bear the classification "ACS grade" meet the specifications set forth by the American Chemical Society. Other chemicals are classified as "analytical reagent grade" or "spectral grade organic solvent." Methods for determining impurities of suspect reagents can be found in Refs. 1-3.

Because even materials of analytical reagent grade vary in quality from lot to lot and manufacturer to manufacturer, reagents must be checked carefully before they are used in the laboratory. Once in service, a reagent should be tested frequently to detect deterioration as early as possible. To maintain reagent quality for as long as possible, the manufacturer's directions for storage and use should be followed closely.

Radioanalytical laboratories require purer chemicals than do other laboratories for many purposes; for example, liquid scintillation requires extremely pure solvents and scintillators to prevent quenching. Trace amounts of impurities that alter counting data without interfering with any chemical procedure must be eliminated (e.g., all traces of radium must be removed from barium used in coprecipitation of radium).

Another difficulty encountered in the radioanalytical laboratory is obtaining radionuclide standards to be used for tracing, testing, and calibration. These standards should be of the highest quality and traceable to the NBS if possible. The EPA standards program mentioned in Section 3 is equally acceptable and is probably better for routine radionuclides. A certificate of calibration must describe the standard adequately and should accompany each radionuclide. The calibration certificate should provide (1) a description of the solution (principal radionuclide, mass or volume, and chemical composition); (2) the reference time and date; (3) the measurement result (activity of principal and possible daughter radionuclides per gram of solution); (4) the measurement method; (5) a statement of purity (list of known or suspected radionuclide impurities, their activities, and how they were measured);

(6) the decay information (statement of the assumed half-life and other decay information); and (7) an estimate of errors (includes errors from the measurements themselves and those created by the decay assumptions).

Calibration standard solutions are shipped in flame-sealed glass ampoules. Once opened, these solutions will deviate rapidly from their calibration values if not properly stored and diluted.

TERMINOLOGY OF QUALITY CONTROL OF DATA

mean: The sum of the test results divided by the number of results taken; that is, $X = \Sigma X_i/n$, where X = mean, X_i = individual result, and n = number of results.

precision: A measure of the reproducibility among replicate observations.

variance: The sum of the squares of deviations of the test results from the mean after division by one less than the total number of results; that is, $VAR = \sum_{i=1}^{n} (\bar{X} - X_i)^2/(n - 1)$.

standard deviation: The square root of the variance; that is,

$$\sigma = (VAR)^{\frac{1}{2}} = \left[\sum_{i=1}^{n} (\bar{X} - X_i)^2/(n - 1)\right]^{\frac{1}{2}}.$$

range: The difference between the highest test result and the lowest test result in a set of observations.

accuracy: A measure of the agreement between observed and accepted values.

systematic error: Errors that may be traced to the personal errors of the experimenter, the instrumental errors of his measuring devices, the errors that repose in the method of analysis he employs, or a combination of these. Accuracy describes this type of variability or error.

random error: The necessity for making estimations is inherent in the process of collecting data for the measurement of any quantity. For this reason, any measurement will be uncertain, in an amount that depends on the relative magnitude of the estimations involved in its evaluation. Careful experimental design can reduce this uncertainty; however, small irreducible variations will remain. Since radioactive decay is a random process, any counting measurement will have a random error associated with it. Precision describes this type of variability or error.

bias: The difference between the average of a set of test results and the accepted value. Bias usually is indicated only when a consistent difference is observed over time and can be corrected for by the application of appropriate correction factors. Bias is a measure of the systematic error.

An excellent discussion of this terminology and its significance to an analytical chemist can be found in Ref. 4.

PERFORMANCE CRITERIA

For a successful quality control program, acceptable and attainable performance criteria must be selected for precision and accuracy. These criteria must reflect the capabilities of the laboratory and the purposes for which the data are to be used.

These criteria can be drawn up initially from experience with the analytical method or from criteria set by other laboratories using the same procedure. A tabulation of allowable deviations used by the EPA in their Environmental Radioactivity Laboratory Intercomparison Studies Program is given in Table 1.[5] As can be seen, the criteria are a function of the particular analysis under study. These values certainly are not the only ones that could be used; however, a laboratory might use these until enough data can be compiled to set its own criteria from experience.

INTERNAL QUALITY CONTROL--DEMONSTRATING PRECISION

A laboratory must be able to reproduce its analytical results internally within acceptable limits. If the laboratory cannot show such consistency, all its results can be considered unsatisfactory. To demonstrate this internal consistency, the laboratory staff should set up a program of duplicate analysis on a portion of the actual sample workload, with properly kept records[6-10]. This technique will also direct the staff to any problems in analytical procedures very quickly.

The best type of duplicate (or replicate) analysis program is one based on blind samples, which denies the analyst any foreknowledge concerning the sample that might bias a second determination. However, conducting such a program in the laboratory is not always easy, especially in those smaller laboratories in which the analyst is aware of every laboratory activity.

In such a case, an alternative approach to a duplicate analysis program can be used, in which one sample out of every ten submitted for a particular analysis is randomly selected for duplicate analysis. All eleven samples, ten unknowns and one duplicate, are analyzed simultaneously so that the data from the analyses are then free of any foreknowledge concerning the expected result. Of course, if less than ten samples are to be analyzed, one of those available is selected as the duplicate.

The laboratory staff must ensure that all duplicates are taken from a homogeneous matrix so that no additional variance is introduced into the duplicate determinations. However, the sample size and the physical and chemical characteristics of the duplicate samples should closely approximate those of samples routinely analyzed singly. Because true duplication of all types of samples is not always possible, spiked samples may have to be substituted.

TABLE 1. LABORATORY PRECISION

One Standard Deviation Value for Various Analyses

Nuclide	Level	Standard deviation (single determination)[a]
^{131}I	5-100 pCi/l or kg	5 pCi/l
	>100 pCi/l or kg	5%
^{140}Ba	5-100 pCi/l or kg	5 pCi/l
	>100 pCi/l or kg	5%
^{137}Cs	5-100 pCi/l or kg	5 pCi/l
	>100 pCi/l or kg	5%
^{89}Sr	5-100 pCi/l or kg	5 pCi/l
	>100 pCi/l or kg	5%
^{90}Sr	2-30 pCi/l or kg	1.5 pCi/l
	>30 pCi/l or kg	5%
^{40}K	$\geq$0.1 g/l or kg	5%
Gross alpha	$\leq$20 pCi/l	5 pCi/l
	>20 pCi/l	25%
Gross beta	$\leq$100 pCi/l	5 pCi/l
	>100 pCi/l	5%
^{3}H	$\leq$4000 pCi/l	$1\sigma = 16985 \times (pCi/l)^{0.0933}$
	>4000 pCi/l	10%
^{226}Ra	$\geq$0.1 pCi/l	15%
^{239}Pu	$\geq$0.1 pCi/l, g, or sample	10%

[a]These limits must be corrected appropriately if multiple determinations are being made.

Source: Environmental Protection Agency. Environmental Radioactivity Laboratory Intercomparison Studies Program, FY 1977. EPA-600/4-77-001; Las Vegas, Nev., January 1977.

Selection of a sufficient number of samples is necessary to determine whether the data meet the established criteria. This selection must be a compromise between the number of results necessary for statistical evaluation and the amount of additional workload the laboratory can perform. The ideal procedure would be to perform duplicate analyses on about 10 percent of the samples processed by the laboratory. This goal may be too high for a laboratory that has a large workload; therefore, 20 sets of duplicate data of each sample analysis type should be considered the minimum amount of data to be statistically analyzed during a reporting period. All laboratories should try to perform duplicate analysis on at least five percent of its samples.

Accurate records should be kept for duplicate analyses. All factors that might affect the analytical performance should be recorded. Information should include at least the date, analyst, and instruments used. Figure 3 is an example of a typical record or log of quality control duplicates.

After these data are collected, a statistical range analysis can be performed. One of the most common analytical techniques currently in use is that suggested by Rosenstein and Goldin,[6] in which a mean range ($\bar{R}$) between duplicate analyses is calculated from the standard deviation of the analysis; this range is a function of concentration (see Table 1). The formula for this calculation is $\bar{R} = d_2\sigma$, where d_2 is a function of the number of replicates involved (see Table 2) and σ is the standard deviation, as derived from Table 1. The control limits can be calculated by $\bar{R} + 3\sigma_R = D_4\bar{R} = D_4 d_2\sigma$, where σ_R is the standard deviation of the range and D_4 is a function of the number of replicates involved. Therefore, $\sigma_R = \bar{R}(D_4-1)/3$. The factors d_2 and D_4 are listed in Table 2 for several different sets of observations. For a range of concentrations, control limits can be calculated and plotted as in Figure 4.

TABLE 2. FACTORS FOR CALCULATING RANGE CONTROL CHART LINES[6]

Number of observations	Central line factor (d_2)	Control limit factor (D_4)
2	1.128	3.267
3	1.693	2.575
4	2.059	2.282
5	2.326	2.115
6	2.534	2.004

QUALITY CONTROL REPLICATE ANALYSIS RECORD

Sample	Determination No. 1				Determination No. 2			
	Date	Counter	Analyst	Result	Date	Counter	Analyst	Result

Figure 3. Example of a typical record or log of quality control duplicates.

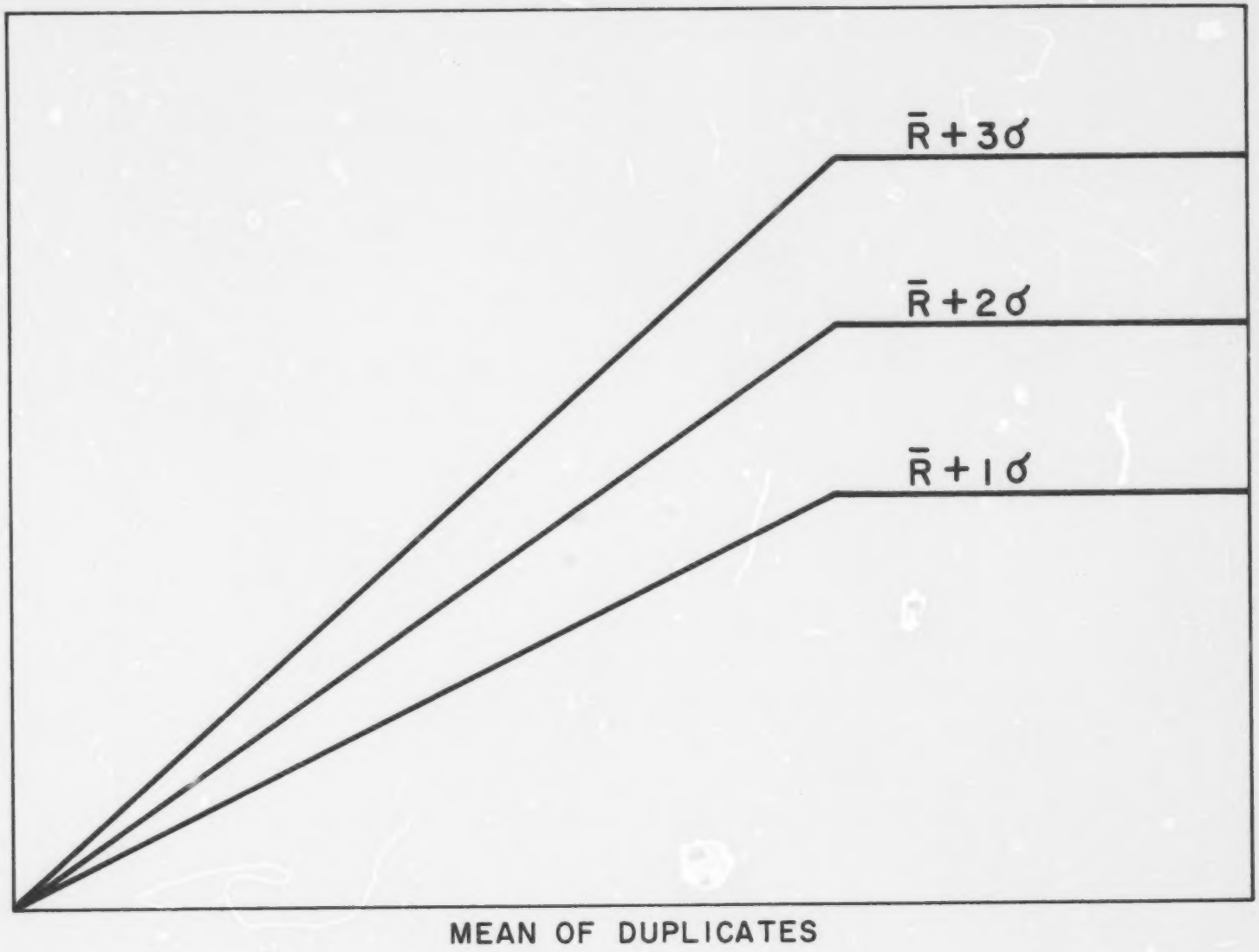

Figure 4. Plot of duplicate range vs. duplicate mean shows the effect of increasing concentration on range values.

Once the range limits are set up, results of the duplicate analyses can be evaluated. The observed range between duplicates is classified as $\leq(\bar{R} + \sigma_R)$, $\leq(\bar{R} + 2\sigma_R)$, $\leq(\bar{R} + 3\sigma_R)$, or $>(\bar{R} + 3\sigma_R)$(see Figure 1). The number of duplicate analyses that fall into each category indicates the laboratory's performance. Theoretically, the distribution should be as follows:

Range	Percent of results
$\leq(\bar{R} + \sigma_R)$	84
$\leq(\bar{R} + 2\sigma_R)$	97.5
$\leq(\bar{R} + 3\sigma_R)$	100
$>(\bar{R} + 3\sigma_R)$	0

Using gross beta data from Table 3 and statistical parameters from Tables 1 and 2, one can perform a sample evaluation. The standard deviation for a single determination is 5 pCi/ℓ; the standard deviation for a duplicate determination is $5/\sqrt{2} = 3.54$ pCi/ℓ. Therefore, $\bar{R} = d_2\sigma = 1.128(3.54) = 3.99$ pCi/ℓ; and $\sigma_R = \bar{R}(D_4 - 1)/3 = (3.99)(3.267 - 1)/3 = 3.01$ pCi/ℓ. From this the range limits may be determined:

$$\leq(\bar{R} + \sigma_R) = \leq 7.00 \text{ pci}/\ell; \quad (1)$$

$$\leq(\bar{R} + 2\sigma_R) = \leq 10.01 \text{ pci}/\ell; \quad (2)$$

$$\leq(\bar{R} + 3\sigma_R) = \leq 13.02 \text{ pci}/\ell; \quad (3)$$

$$>(\bar{R} + 3\sigma) = < 13.02 \text{ pci}/\ell. \quad (4)$$

Therefore, 29 duplicate measurements result in the following distribution:

	Results	
Range	Number (n=29)	Percentage
$\leq(\bar{R} + \sigma_R)$	26	90
$\leq(\bar{R} + 2\sigma_R)$	2	97
$\leq(\bar{R} + 3\sigma_R)$	1	100
$>(\bar{R} + 3\sigma_R)$	0	0

This agrees very favorably with the theoretical distribution shown earlier.

TABLE 3. GROSS BETA IN WATER (pCi/ℓ) DUPLICATE ANALYSIS DATA

Sample number	First determination				Second determination				
	Date	Counter[a]	Analyst	Result	Date	Counter[a]	Analyst	Result	
1	10/22	LB	B	1.7	10/22	LB	B	2.0	0.3
2	10/22	LB	B	2.3	10/22	LB	B	2.7	0.4
3	10/28	LB	C	1.9	10/28	LB	C	2.2	0.3
4	11/4	LB	A	9.7	11/4	LB	A	1.4	8.3
5	11/17	LB	B	4.5	11/17	LB	B	3.1	0.2
6	11/19	LB	B	3.3	11/19	LB	B	3.1	0.2
7	12/3	WB	C	3.5	12/3	WB	C	3.2	0.3
8	12/22	LB	C	3.7	12/22	LB	C	4.4	0.7
9	1/4	WB	C	1.0	1/4	WB	C	3.1	2.1
10	1/10	WB	B	23.7	1/10	WB	B	12.2	11.5
11	1/12	LB	A	1.8	1/12	LB	A	2.1	0.3
12	1/18	LB	A	1.9	1/18	LB	A	2.5	0.6
13	1/18	WB	C	4.3	1/18	WB	C	4.5	0.2
14	1/20	WB	C	7.7	1/20	WB	C	6.8	0.9
15	1/25	LB	B	0.9	1/25	LB	B	0.6	0.3
16	1/31	LB	C	1.0	1/31	LB	C	1.6	0.6
17	2/10	LB	C	54.7	2/10	LB	C	55.5	0.8
18	2/13	LB	C	2.7	2/13	LB	C	0.9	1.8
19	2/15	WB	B	6.9	2/15	WB	B	0.1	6.8
20	2/27	WB	B	2.1	2/27	WB	B	2.3	0.2
21	3/15	WB	C	7.2	3/15	WB	C	6.8	0.4
22	3/17	LB	A	2.7	3/17	LB	A	2.6	0.1
23	3/20	WB	B	5.8	3/20	WB	B	4.2	1.6
24	3/25	LB	B	2.3	3/25	LB	B	2.5	0.2
25	3/30	LB	A	2.4	3/30	LB	A	3.3	0.9
26	4/2	WB	C	11.1	4/2	WB	C	4.0	7.1
27	4/4	LB	A	4.1	4/4	LB	A	4.1	0.0
28	4/8	LB	A	1.9	4/8	LB	A	4.0	2.1
29	4/17	LB	C	52.0	4/17	LB	C	51.1	0.9

[a]LB = Beckman Low Beta II; WB = Beckman Wide Beta II.

Interpretations of observed results can yield several possibilities:

1. An acceptable distribution will either be close to that predicted by theory or shifted toward the σ_R and the $2\sigma_R$ categories.

2. An unacceptable distribution will be shifted toward the $2\sigma_R$, $3\sigma_R$, and $>3\sigma_R$ categories.

3. An "outlier" distribution follows the theoretical distribution, but has a few results in the $>3\sigma_R$ category. This indicates acceptable precision with occasional poor results. However, these others should be examined closely to determine source because important knowledge of weaknesses in the analytical system may be discovered.

These results may be used as a basis for further study of the analysis system. However, the occurrence of an unacceptable distribution requires that immediate steps be taken to correct the situation causing the poor analytical results.

INTERNAL QUALITY CONTROL--DEMONSTRATING ACCURACY

A laboratory can establish the accuracy of its data by preparing special standard samples containing known concentrations (spikes) of the nuclides of interest and statistically studying the relation between the resulting analytical values and the known concentrations. These spikes should be analyzed regularly so that the laboratory has a running account of its analytical ability.

This type of study requires quadruplicate analyses. The mean of the determinations is calculated from the collected data, and the mean values and individual values then are plotted on control charts.

Means Control Chart

The means control chart enables one to determine the amount of bias between the mean and the expected value. A basic assumption is that the resulting data will resemble a normal distribution over time. When preparing such a control chart (Figure 5), one assumes the known activity to be the mean. The allowable standard deviation for the individual determinations is selected as for the duplicate studies (see Table 1); the standard deviation of the mean is calculated by dividing the standard deviation of the individual measurements by the square root of the number of determinations ($\sigma_m = \sigma/\sqrt{n}$). Acceptable results should fall within $\pm 2\sigma_m$ for 95 percent of the results. Any bias will show up as a consistent displacement of results from the mean.

Individual Results Control Chart

The control chart for individual results (Figure 6) is essentially the same as the means chart except that individual values, rather than the mean, are used. This chart can show the actual effect of the individual results on the mean values. In this chart the standard deviation

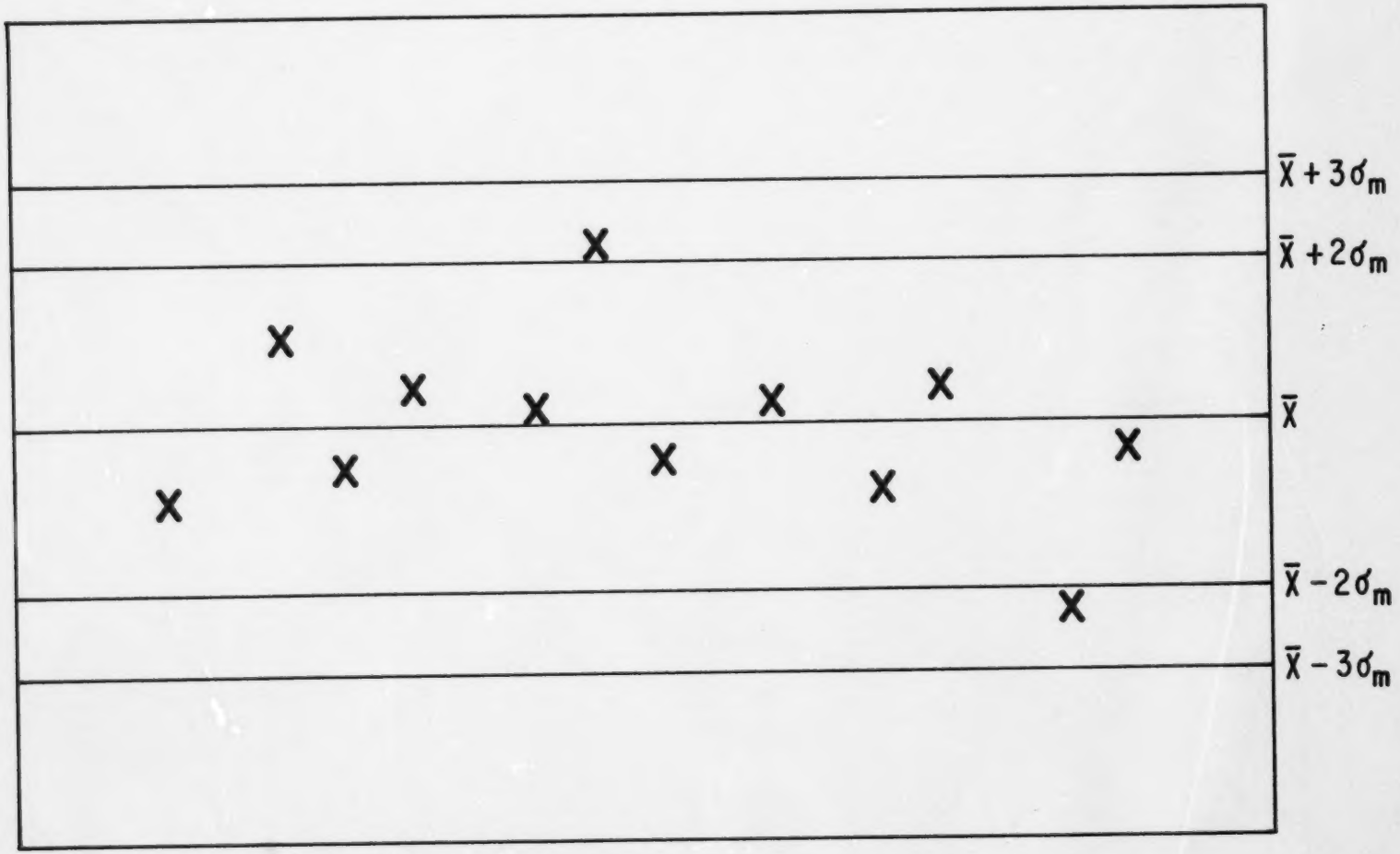

Figure 5. Means control chart. $\bar{X}$ is mean, $\sigma = \sigma/\sqrt{n}$, the ordinate is concentration, and the abscissa is time.

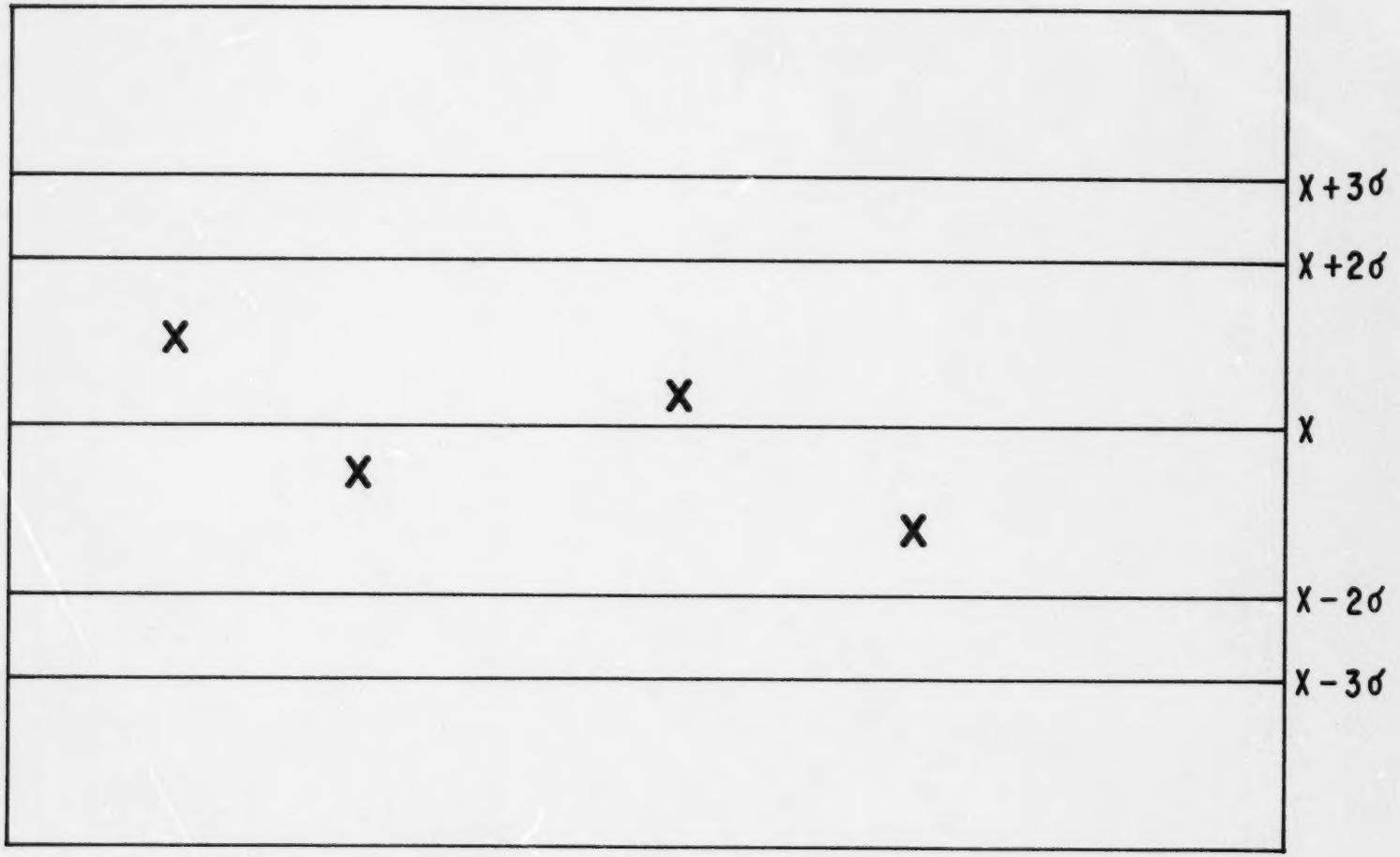

Figure 6. Individual results control chart. X is the known concentration (ordinate), σ is the standard deviation, and the abscissa is the run number.

for the individual results, rather than for the mean, is used. Again, the known value is assumed to be the central value.

A control chart for range also could be developed for use in these statistical analyses; however, the range values determined from the duplicate analyses program should describe the precision of the laboratory adequately. Control charts for individual analysts and counters may also be set up to break down the variables even further.

EXTERNAL QUALITY CONTROL--DEMONSTRATING ACCURACY

An internal program for testing accuracy should not be considered sufficient for documentation. Participation in collaborative testing programs with other laboratories is the best way for a laboratory to evaluate its performance with respect to that of others.

The EPA conducts an Environmental Radioactivity Laboratory Intercomparison Studies Program in which all environmental laboratories should participate. This program provides a large number of different crosschecks regularly. Results from crosschecks are sent to EPA within four weeks after receipt of the samples. After all results are tabulated, the EPA prepares a statistical analysis of the data for each participant that shows its performance with respect to the known values and the performance of other participants. At this time, over 100 laboratories participate in these studies to identify problems with procedures and instruments and to demonstrate analytical accuracy.

Although other agencies, such as the International Atomic Energy Agency, conduct crosscheck programs, most are not nearly as comprehensive as the EPA program.

Programs of split-sample analysis between two or more independent laboratories can also help establish analytical credibility and identify analytical problem areas. In such a program, actual environmental samples are collected and processed; thus, portions of the samples are sent to one or more other laboratories for analysis. This type of program is the only way for an environmental laboratory to estimate the accuracy of its results at true environmental levels. Programs such as those conducted by EPA cannot be carried out at the low levels found in the environment and therefore do not substitute for a split-sample program.

SUMMARY

If a laboratory conducts routine assessments of its precision and accuracy, documentation of the quality of its work is possible. Also, attention can be focused rapidly on analytical problems that otherwise would go undetected. Therefore, quality control must be built into the laboratory program just as any other aspect of analysis is incorporated into the program.

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SECTION 5

DATA HANDLING AND REPORTING

GENERAL

After the laboratory has established control over sample collection, instrumentation, and analytical methods, the remaining aspect of producing useful and accurate data on all samples is the handling and reporting of data produced in the laboratory.

Prescribed procedures must be set up and controlled for the passage of samples through the laboratory to ensure that the proper analyses are assigned and completed. Control measures should be adopted to ensure that correct values are reported for each analysis; the values themselves must have a consistent form and be free of mathematical error.

ANALYTICAL PROCESS

A system for controlling the passage of samples through the laboratory must be established. Because the procedure described here may not answer the needs of every laboratory, each laboratory should develop its own methods according to its own needs and document these methods in written procedures. A general outline of a sample-handling process is described as follows.

1. As they arrive, samples are recorded in a logbook. At this time, a laboratory number is assigned to the sample, and all descriptive information concerning the sample, including sample source, sample, quantity, collection time, and sample collector is recorded.

2. An analytical request sheet, which lists the sample number and descriptive information about the sample, is prepared for the sample. All necessary pretreatments and analyses to be performed should appear on the sheet. Space is provided for completion dates.

3. As results are completed, more information, such as the name of the analyst who performed the work, his calculations for the sample, and all pertinent data that would allow recalculation of results at a later time if necessary, is noted on the result sheets.

4. As various analyses are performed and results are reviewed by the analyst, the request sheet is checked off and the result sheets are attached to the analytical request sheet.

5. After all analyses are completed, the results are sent to the laboratory supervisor or person responsible for reporting results. After the results are reviewed, they are transferred to a final report form.

6. The analysis request form and result sheets are appropriately filed for future reference. Several years of results should be kept for ready reference.

This procedure will allow data to be tested for adequacy at any point during the analysis and to be reexamined at any future time. The data are reviewed thoroughly several times by designated personnel, starting with the senior analyst, before being reported in final form.

In any analytical program, a senior analyst should be responsible for recognizing anomalous results and discussing these with the appropriate persons so that a sample can be reanalyzed before it is discarded or a significant amount of time has passed.

DATA

Although calculations, whether performed by hand, calculator, or computer, usually can generate more digits than are actually needed, valid digits often are thrown away. For this reason the proper use of significant figures should be emphasized.[1,2] A brief list of rules can be given for these evaluations.

1. Final zeros in a whole number may or may not be significant. In the measurement 1800 mm, do the zeros signify that the length was measured to 1 mm or do they merely locate the decimal point (i.e., to distinguish 1800 from 18 mm)? To avoid confusion in cases of this type, use a larger unit. If one chooses the meter as the unit, then 1800 mm becomes 1.8, 1.80, or 1.800 m, depending on the accuracy of the measurement.

2. Zeros before a decimal point with other preceding digits are significant. With no preceding digits, a zero before the decimal point is not significant. For example, in the measurement 150.12, the zero is significant, but in the measurement 0.12, the zero is not significant.

3. If there are no digits preceding a decimal point, the zeros following the decimal point but preceding other digits are not significant; these zeros only indicate the position of the decimal point. Thus, in the measurement 0.050015 kg, the first two zeros are not significant and serve only to locate the decimal point; however, the zeros between 5 and 1 are significant.

4. Final zeros after a decimal point are always significant figures. A weight such as 7.530 g indicates that the measurement was made to the nearest milligram.

5. To round off a figure, if the digit following those to be retained is less than 5, the digit is dropped and the retained digits are not changed.

6. To round off a figure, if the digit following those to be retained is greater than 5, the digit is dropped and the last retained digit is raised by 1.

7. To round off a figure, if the digit following those to be retained is 5 and there are no digits following it except zeros, then the last retained digit is raised by 1 if it is odd and kept unchanged if it is even.

Good books concerning quantitative analysis should be consulted for discussion of how to propagate rounding through arithmetic calculation as well as detailed discussion on the rules above. Generally, analytical results should not be reported to more than four significant figures.

ERRORS CAUSED BY COMPUTATIONAL PROCESSES

Two types of errors, rounding and truncation, may occur in any numerical process.

Truncation errors result from the necessary termination of an otherwise naturally infinite (or very lengthy) process. In most computations, it is neither possible nor necessary to carry an infinite number of significant figures. Therefore, certain classes of numbers, functions, or constants will never be used with exact accuracy. Included are irrational numbers ($\sqrt{2}$), transcendental numbers (π or e) or functions (logarithm, exponential, sine), and fractions that have no terminating representation. With regard to this last category, fractions that have an exact representation in one number base may not possess this property in another. For example, in the decimal system used in manual calculations and by the majority of hand-held and desktop calculators, the fraction 1/10 is accurately expressed as 0.1. In the binary system used by most large-scale computers, however, the fraction has no terminating representation and cannot be expressed exactly. Therefore, the sum of 10 numbers, each expressed as binary representation of 0.1, will not necessarily result in 1.0.

Rounding and chopping (truncation) errors are generally considered to be a troublesome problem when using a computer. By rounding, we refer to the symmetrical rounding procedure discussed previously. Rounding may best be compared with the chopping process by an example: As the result of some numerical operation, we obtain the number 0.41877 and wish to express it to four significant digits; by rounding, 0.41877 becomes 0.4188, but by chopping, 0.41877 becomes 0.4187. In chopping, the digits beyond those that have been declared significant are ignored and have no effect on the final resulting number.

Because computers generally have a fixed word length and cannot express any number with infinite precision, some decision must be made as to what to do when the limits of precision within the computer are reached. A large number of FORTRAN compilers do, in fact, set up the object program to use chopping, which introduces less error in the

calculated result than the familiar rule for rounding. In addition, the use of the familiar symmetrical rounding procedure in every arithmetic operation, including the many places in a program in which it is not really necessary, would waste computer time.

For computers and calculators, rounding and chopping may introduce errors not only in internal calculations, but also in displayed or printed output. While the machine internally may carry out arithmetic operations with precision ranging from 8 to 16 decimal digits, this degree of precision is generally not necessary for display or printout of final results. For straight-line calculations, rounding or chopping the final answer to four significant figures may introduce a relative error that is greater by several orders of magnitude than any error accumulated during the calculation. Also, chopping of the final displayed result by the computer does introduce more error in the displayed decimal than would rounding.

Recursive or iterative operations suffer more from the effects of rounding or chopping than do straight-line calculations. This problem is typified in the resolution of multicomponent gamma ray spectra, where a set of simultaneous equations must be solved. In general, there are two types of numerical techniques for solving simultaneous equations: direct methods, which are finite (Gaussian elimination), and indirect methods, which are infinite (iterative techniques). Obviously, no practical technique can actually be infinite; what is meant is that the direct methods will produce, in principle (neglecting rounding errors), an exact solution, if one exists, in a finite number of arithmetic operations. An indirect method, on the other hand, would in principle require an infinite number of arithmetic operations to produce an exact solution. That is, an indirect method has a truncation error, whereas a direct method does not.

Rounding errors may not be neglected. In a large, ill-conditioned system, the rounding errors in a direct method may make the solution meaningless; the magnitude of the final error may, in severe cases, be larger than the derived result. Therefore, in spite of its truncation error, an indirect method may be much more desirable because the problem of accumulated rounding error is minimized.

DATA STORAGE

If the analytical data reported by the laboratory have as their final destination a computerized data base, then a great deal of care must be exercised to ensure that no transcription errors are generated. Because every transposition of data increases the possibility of such errors, the number of intermediate transcriptions of data should be limited. Procedures should be set up for random checking of the data base to ensure the quality of the stored data.

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SECTION 6

STATISTICS AND COUNTING DATA

GENERAL

Statistics, as a science, deals with probability. Probability is a useful concept in all areas of science because no two analyses or measurements give identical answers. Measurements of radioactivity are bound even more closely to statistical evaluation because of the random nature of the disintegration process. The basic laboratory question is how to determine, from a few measurements or a single measurement, the best approximation to a "true" value.

The goal of this manual has been to examine areas and to demonstrate methods that can be used to reduce systematic errors to the point that only the small unavoidable fluctuations of random error are present. Of course, every analytical result still has a degree of uncertainty. These uncertainties arise from all the measurement processes involved in the analysis, such as weighing, volumetric processes, and counting error. An analyst must try to estimate this error (uncertainty) for each single analysis by propagating the random error in all measurements for each individual sample. Measuring radioactivity involves a statistical evaluation of counting measurements to estimate these uncertainties and reduce them to as small a figure as possible.

The lower the level of activity in a sample, the more difficult it is to distinguish the activity of the sample measurement from statistically allowable fluctuations in the background. To evaluate sample measurements, one must be able to estimate the sensitivity of the analysis, which is sometimes called lower limit of detection (LLD) or minimum detectable activity (MDA). This section describes how sensitivities can be estimated for some analytical methods.

This section by no means is a treatise on statistics.

COUNTING STATISTICS

Two types of statistical distributions are used most often in the radioanalytical laboratory: (1) The Gaussian, or normal, distribution is used to describe continuous variables, and (2) the Poisson distribution applies to discrete variables.[1-4]

The form of the Gaussian distribution for n measured values is

$$f(x) = \frac{1}{\sigma_x\sqrt{2\pi}} \exp \left[- \frac{(x - \mu)^2}{2(\sigma_x)^2} \right] , \qquad (5)$$

where μ = mean of the measurement values (x) ,

σ_x = standard deviation = $[\Sigma(x - \mu)^2/(n - 1)]^{\frac{1}{2}}$.

This equation describes a bell-shaped curve, any area under which is related to the probability of a particular result. This area is often divided into ranges of σ_x about the mean, μ. Thus,

Area	Probability
$\mu \pm \sigma_x$	0.683
$\mu \pm 2\sigma_x$	0.955
$\mu \pm 3\sigma_x$	0.997

This division into regions is the source of terms such as 2σ, 2 sigma level, and 95 percent confidence level. Gaussian statistics are used in the radioanalytical laboratory to describe the behavior of multiple measurements of a single value.

Multiple measurements are seldom possible for most work performed in the radioanalytical laboratory. Availability of instruments for repeated countings is too expensive to maintain. For this reason, the use of Poisson statistics can allow an estimate of behavior from a single measurement.

The form of the Poisson distribution is expressed as

$$f(x) = \frac{(e^{-\bar{x}})(\bar{x})^x)}{x!} \quad , \qquad (6)$$

where $x = 0, 1, 2, \ldots,$

$\bar{x}$ = estimated mean.

The standard deviation, s, for the estimated mean is $\sqrt{\bar{x}}$.

EXAMPLE 1: A standard check source was counted to determine the counter efficiency. The following one-minute counts were observed: 7747, 7738, 7840, 7785, 7705, 7667, 7812, 7827, 7623, and 7739. The total count was 77483, and the mean was calculated to be $\mu = 77483/10 = 7748$. Thus, for the Gaussian distribution,

$$\sigma = [\Sigma(x - \mu)^2/(n - 1)]^{\frac{1}{2}} = 70, \qquad (7)$$

and for the Poisson distribution,

$$s = \sqrt{\bar{x}} = 88. \qquad (8)$$

The agreement of the two estimates indicates that the counting proceeded satisfactorily. The Gaussian estimate and the Poisson estimate should be approximately the same. The agreement of the results also shows that the Poisson estimate is a quick but satisfactory measure of counting data.

For situations in which the standard deviation is of the same order of magnitude as the mean, the distribution of data will be markedly non-Gaussian, and Gaussian probability levels and also propagation of errors give grossly biased answers. The only way to eliminate the bias is a very tedious trial-and-error use of the Poisson distribution itself.

The Poisson standard deviation often appears as slightly different expressions from that shown above when converted to a counts-per-minute (counts/min) figure:

$$s_{\text{counts/min}} = \sqrt{\bar{x}}/t$$

$$= \sqrt{R/t} \quad , \qquad (9)$$

where t = counting time,

R = counting rate.

PROPAGATION OF ERRORS

If all radioanalytical analyses involved only one counting measurement, estimating the uncertainty of a final result by applying Poisson statistics to obtain a standard deviation would be quite simple. However, this is seldom, if ever, the case since almost all counting data must be corrected for background contributions. Both the sample and background counts have uncertainties that must be reflected in the final result. The theory of propagation of errors can be applied to estimate the reliability of the final calculated result.[5,6]

If $Q = f(X,Y,\ldots)$, where $X,Y,\ldots$ are independent, normally distributed variables, the asymptotic uncertainty (variance) in Q resulting from uncertainties in $X,Y,\ldots$ is given by the expression

$$\sigma_Q^2 = (\partial Q/\partial X)^2\sigma_x^2 + (\partial Q/\partial Y)^2\sigma_y^2 + \ldots \qquad (10)$$

The standard deviation for Q is found by taking the square root of the expression. For the specific case of the error of difference between two counting determinations ($Q = X - Y$), the proper equation is

$$\sigma_Q = (\sigma_s^2 + \sigma_B^2)^{\frac{1}{2}} \quad , \qquad (11)$$

where σ_Q = error of the difference,

σ_s = estimated standard deviation for the sample,

σ_B = estimated standard deviation for the background.

Formulas for other simple functions are shown in Table 4.

TABLE 4. FORMULAE OF PROPAGATION OF ERROR FOR SOME SIMPLE FUNCTIONS

Function	Error formula
$Q = X \pm Y$	$\sigma_Q = (\sigma_x^2 + \sigma_y^2)^{\frac{1}{2}}$
$Q = aX \pm bY$	$\sigma_Q = (a^2\sigma_x^2 + b^2\sigma_y^2)^{\frac{1}{2}}$
$Q = XY$	$\sigma_Q = XY(\sigma_x^2/X^2 + \sigma_y^2/Y^2)^{\frac{1}{2}}$
$Q = XY$	$\sigma_Q = X/Y(\sigma_x^2/X^2 + \sigma_y^2/Y^2)^{\frac{1}{2}}$
$Q = X^n$	$\sigma_Q = n(X^{n-1}\sigma_x)$
$Q = \ln X$	$\sigma_Q = \sigma_x/X$
$Q = \log X$	$\sigma_Q = 0.434\sigma_x/X$

Sources: Overman, R. T., and H. M. Clark. Radioisotope Techniques. McGraw-Hill Book Co., New York, 1960. 476 pp.

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EXAMPLE 2: A sample counted for 50 minutes gave a gross count of 123 counts; the background for the same period was 68 counts. The error of the net count is shown below:

$$\sigma_s = 123^{\frac{1}{2}} = 11.09 \qquad (\sigma_s^2 = 123) \; ; \qquad (12)$$

$$\sigma_B = 68^{\frac{1}{2}} = 8.25 \qquad (\sigma_B^2 = 68) \; ; \qquad (13)$$

$$\sigma_Q = (68 + 123)^{\frac{1}{2}} = 13.82 \; . \qquad (14)$$

Therefore, the net count is 55±14.

A more common expression for this error term, when both a sample measurement and background measurement are involved, is

$$\sigma_Q = (R_s/t_s + R_B/t_B)^{\frac{1}{2}}, \qquad (15)$$

where R_s = gross sample counting rate,

R_B = background counting rate,

t_s = sample counting time,

t_B = background counting time.

EXAMPLE 3: A sample counted for 50 minutes gave a gross count of 137 counts. The background for a 10-minute count was 15 counts.

$$\sigma_Q = \left(\frac{137/50}{50} + \frac{15/10}{10}\right)^{\frac{1}{2}} \qquad (16)$$

$$= (0.055 + 0.15)^{\frac{1}{2}} = (0.205)^{\frac{1}{2}}$$

$$= 0.45 \text{ counts/min.}$$

Therefore, the net counting rate is 1.74±0.45 counts/min (neglecting significant figures). Because the gross counting rate is the sum of the background and sample counting rates, the background will dictate the precision of the final answer if background and sample counting times are equal. Therefore, counting times must be selected to minimize the background contribution to the error term.

Several possibilities exist for reducing the counting error for a particular analysis: (1) increasing the counter efficiency; (2) increasing the sample size; (3) increasing the counting time; and (4) lowering the background. Increasing the efficiency or sample size gives the greatest benefit since these terms are applied directly in all final calculations. Possibilities (3) and (4) vary with the square root and therefore yield a lesser reduction in the size of the error term.

When using background measurements in analytical calculations, a figure representing the background over a long period of time, rather than figures from daily measurements, is preferable. For example, background of 1.27±0.10 counts/min averaged over a year is a much better value for calculation purposes than a value of 1.33 counts/min determined for a particular day. Although using a long-term average in calculations will tend to smooth out fluctuations, an average figure should not, of course, be used when a radical change in background has occurred.

A test often used to evaluate instrument background measurements to determine whether the instrument is performing as statistically expected is the Chi-square test, in which Chi-square (χ^2) is calculated by

$$\chi^2 = \left[\sum_{i=1}^{n} (x_i - \bar{x})^2\right]/\bar{x}, \qquad (17)$$

where x_i = individual result,

$\bar{x}$ = average of all the measurements.

Values of Chi-square have been calculated and tabulated for the number of values measured.

Number of measurements	Allowed χ^2 limits
5	0.3 - 13
10	2 - 22
15	4 - 29
20	7 - 36
30	14 - 50

A value outside the limits indicates that the instrument is not performing as expected from statistical considerations.

LIMITS OF DETECTION

An examination of equation (15) shows that the percent error increases as the gross counting rate approaches the background counting rate. Neither the gross counts nor the background counts are hard, fast numbers; instead, they are members of two distributions that begin to overlap when the sample has very low amounts of activity above background. Estimating the reliability of the difference between the two measurements becomes a complex problem when overlap occurs.

Several methods for estimating the LLD or MDA in radioanalytical measurements have been proposed.[6,7] The method most commonly used assumes that, unless the gross counting rate is greater than the background counting rate plus two standard deviations, the amount of activity contained in the sample is less than detectable.

EXAMPLE 4: A low-background beta counter has an average background of 64 counts in 50 minutes measured over a period of a year.

$$s = \sqrt{\bar{x}} = \sqrt{64} = 8, \tag{18}$$

$$2s = 16 \text{ counts.}$$

In this example, the gross counts must exceed 80 counts in 50 minutes to give 95 percent confidence that there is actually any activity present in the sample.

Another approach to this problem is presented in Refs. 8 and 9. This procedure uses a statistical technique known as hypothesis testing, in which two types of error are assumed to be possible: (1) concluding that there is sample activity when there is none (Type I error) and (2) concluding that there is no sample activity when there is some (Type II error). The terms alpha (α) and beta (β) represent Type I and Type II, respectively; alpha is usually allowed to be 5 percent (0.05) and beta is usually set at 5 percent (0.05). The LLD is then approximated as

$$LLD \simeq (k_\alpha + k_\beta)s_o \quad , \tag{19}$$

where k_α = the value of the upper percentile of the standardized normal variate corresponding to the preselected α,

k_β = the corresponding value for the predetermined degree of confidence for detecting the presence of activity $(1 - \beta)$,

s_o = the estimated standard error for the net sample counting.

If the values of α and β are set at the same level (0.05) and the sample and background counts are close, as would be the case at the LLD, other approximations also may be made. If

$$s_{net} = \sqrt{s_s{}^2 + s_B{}^2} \simeq \sqrt{2}\, s_B, \tag{20}$$

and

$$k = k_\alpha = k_\beta \, , \tag{21}$$

then

$$LLD = 2\sqrt{2}\, ks_B \, . \tag{22}$$

α	$1 - \beta$	k
0.01	0.99	2.327
0.02	0.98	2.054
0.05	0.95	1.645
0.10	0.90	1.282
0.20	0.80	0.842

For the previous example, we can calculate the LLD by this method using $\alpha = \beta = 0.05$ to find the background variance:

$$LLD = 2\sqrt{2}\ ks_B \ ; \tag{23}$$

$$s = \sqrt{\bar{x}} = \sqrt{64} = 8 \ ; \tag{24}$$

$$LLD = 2\sqrt{2}\ (1.645)(8) \simeq 37 \text{ counts.} \tag{25}$$

This value is the number of net counts above background that must be observed before one can report a result above LLD. Note that this is a more conservative estimate of the LLD than that shown in example 4. This method of LLD calculation is becoming the most accepted procedure.

This 95 percent confidence criterion is a very rigorous one. A more liberal criterion might be to allow a 20 percent chance of erroneously reporting activity when none is actually present and to keep the 5 percent requirements for not reporting activity when it is actually present. This change in criteria would lead to the following expression:

$$LLD = (k + k)\ \sqrt{2}\ s_B \tag{26}$$

$$= (1.645 + 0.842)\ \sqrt{2}\ s_B$$

$$= (2.487)\ \sqrt{2}\ s_B$$

$$= 3.52 s_B \ .$$

For the previous example, the LLD calculated by this method would be 28 net counts.

The extraction of results from allowable variations can be difficult and always introduces a degree of uncertainty in the final result. This final result must be measured in light of the LLD levels before attaching meaning or significance to the value. Allowable variations and LLD levels also must be considered when formulating quality control analysis of laboratory data.

Many other authors[10-12] have approached the problem of LLDs with reference to radioanalytical measurements.

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The first four references are general in nature and apply to all areas of statistics involved in radiochemistry.

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SECTION 7

HANDLING STANDARDS OF RADIOACTIVITY

GENERAL

Every laboratory involved in radioanalytical determinations uses radioactive standards for calibration and procedures testing. The first requirement is to acquire standards that are well characterized and documented. After standards are received, they should be properly stored and diluted to ensure that the standardization is not invalidated by improper handling.

STORAGE OF STANDARD SOLUTIONS OF RADIOACTIVE MATERIALS

There are several ways in which the calibration of a radioactivity standard can change by 10% or more. Because degradation of a standard is often difficult to detect, it should be avoided by compliance with proper handling procedures. The most common ways by which the standardization may change are (1) adsorption of trace metals on the walls of the container, (2) precipitation, (3) loss of water by evaporation, (4) biological activity in the solution, and (5) radioactive decay.

Adsorption or precipitation is prevented by the addition of acid, complexing agents, or carriers to the solutions. The supplier of the standard should furnish the chemical composition of the nuclide solution with his certification. Radionuclide standards should not be stored in plastic bottles for more than a few days since water can evaporate through the bottle walls; storage in glass bottles is preferred. To prevent the growth of biological material in standards, add a few drops of either formaldehyde or chloroform. Standards should not be used beyond four half-lives of the radionuclides.

DILUTION OF STANDARD SOLUTIONS

Standard radionuclide solutions usually are calibrated by weight. Since weighing is more accurate and normally more convenient than measurements by volume, weighing is the preferred method for diluting standards. An additional benefit of this method is the fact that weighing eliminates the necessity of making density corrections when acid or carrier is present.

All normal weighing precautions should be exercised when preparing standards. Special consideration should be taken to ensure that thermal equilibrium and constant weights are obtained.

The volumetric flask used for the dilution should be rinsed carefully with the diluting solution containing carrier, acid, or complexing agent and then partially filled. After the standard solution is pipetted accurately into the flask, additional diluting solution is added to bring

the flask to the mark. The flask then should be sealed with a stopper of ground glass, and the solution should be mixed thoroughly. When the solution is not being used, the stopper should be kept in place to prevent evaporation.

Pipets used for these standards can be either lambda (μℓ) pipets made of glass or fixed-volume pipets with disposable tips. The glass pipets should be stored and cleaned separately from other pipets used in the laboratory to prevent contamination. Each pipet should be labeled to identify the radionuclide for which it has been used in the past.

USING CALIBRATED SOURCES

The accuracy with which the half-life and purity of the source are known will affect the accuracy of calculations when certified emission rates are used. Also, knowledge of the calibration geometry, instrumentation, and efficiencies occasionally may be necessary.

The rate of emission from the surface of a solid source may not be the same as the disintegration rate. The possible existence of a complex decay scheme for the nuclide and the phenomena of adsorption and scattering of radiation within the source both affect this relationship.

Variations in shape, size, or composition between a calibrated source and the source to be measured may imply different detection sensitivities for the two sources because of the possible differences in adsorption or scattering of radiation. These effects must be minimized and accounted for in estimating the accuracy of the unknown source.

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